LXVIII.—*Some Homonucleal Tri-derivatives of Naphthalene.*

By Raphael Meldola, F.R.S., and C. H. Desch.

When parabromo-α-acetonaphthalide is nitrated in acetic acid solution, it readily forms a homonucleal mononitro-derivative (Liebermann and Scheiding (*Annalen*, **183**, 258). The nitro-group is ortho- to the acetamido-group in this compound, as is shown by its yielding an anhydro-base on reduction (Meldola, Trans., 1885, **47**, 505).* The nitrobromo-α-acetonaphthalide is easily and quantitatively hydrolysed into the nitrobromo-α-naphthylamine,

$$NH_2 : NO_2 : Br = 1 : 2 : 4,$$

by means of sulphuric acid (*ibid.*, p. 500).

* At the time of the researches above referred to, I was led to the conclusion that when the mixed nitro-derivatives obtained by nitrating α-acetonaphthalide in acetic acid (Liebermann's method) are brominated, it is the paranitro-compound only which is attacked. This conclusion was based on a supposed isomerism of the nitrobromo-derivative, which apparently differed in melting point from Liebermann's. But the isomerism was more especially inferred from the observation that the dibromonaphthylamine obtained from this compound by hydrolysis, replacement of NH_2 by H, reduction, acetylation, bromination, and hydrolysis gave a bromophthalic acid by oxidation (*loc. cit.*, p. 511). Liebermann and Scheiding's compound by similar treatment gave a dibromonaphthylamine which gave doubtful results on oxidation (*loc. cit.*, p. 515). Both dibromonaphthylamines gave the same dibromonaphthalene by the diazo-reaction. I had always intended to repeat these experiments in order to clear up the discrepancy, but as my colleague, Dr. Armstrong, was engaged in a detailed study of the naphthalene derivatives with a view to settle the

Some years ago experiments were commenced by one of the authors of this note with the object of ascertaining whether in homonucleal tri-derivatives the hydrogen in the second β-position could be substituted by NO_2, so as to produce homonucleal tetra-derivatives from which the missing di-β-quinone might possibly be prepared. It was thought that if the quinone itself could not exist, its di-haloïd derivatives of the type $C_{10}H_4Br_2O_2$ [Br : O : O : Br = 1 : 2 : 3 : 4] might be more stable. The discovery of tetrabromo- and tetrachloro-ortho-benzoquinone by Zincke in 1887 (*Ber.*, **20**, 1776) gave encouragement to continue the work in this direction. As a preliminary step, it was attempted to replace the amido-group in the nitrobromonaphthylamine by bromine by decomposing the diazoperbromide, $C_{10}H_5Br(NO_2)\cdot N_2\cdot Br_3$, in the usual way. It was found, however, that by this method the nitro-group was also replaced by bromine, and the product consisted only of the tribromonaphthalene (m. p. 113—114°) previously described by one of us (Trans., 1883, **43**, 4). About the same time, and quite independently, the same result was announced by Prager (*Ber.*, 1885, **18**, 2163). This author further stated in his paper that the amido-group in the nitrobromonaphthylamine could not be replaced by bromine by Sandmeyer's modification of the diazo-reaction. Accepting Prager's statement as correct, the experiments were accordingly abandoned.

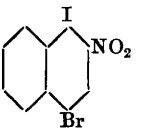
orientation of the substituents in the di- and tri-chloro and di- and tribromo-derivatives, this field was left to him. In a recent communication by Armstrong and Rossiter (Proc., No. 104, **7**, 186), these authors have shown that the product of the action of bromine on the mixed nitro-α-acetonaphthalides is identical and not isomeric with Liebermann and Scheiding's compound, and that it is therefore the ortho- and not the para-compound which is attacked, as I had originally supposed. They have also shown that the two bromonaphthalenes are identical, being the 1 : 4-modification (m. p. 82—83°). These results, which I have since repeated with the assistance of Mr. E. M. Hawkins, and can now corroborate, are instructive as enforcing the conclusion to which I was led seven years ago, that in the study of isomeric naphthalene derivatives, melting points are of little or no value (*loc. cit.*, p. 516). All subsequent experience has confirmed this. It appears also that oxidation with nitric acid gives very uncertain information respecting the homo- or heteronucleal character in many cases. These and other difficulties which the investigator of naphthalene derivatives has to guard against are pointed out by Armstrong and Rossiter in another note (Proc., No. 104, **7**, 182). The effect of the revision of the work by these authors is to remove my bromonaphthylamine (m. p. 62°) and its derived compounds from the list of naphthalene derivatives. I am glad of the present opportunity of preventing the perpetuation of these compounds in chemical literature. I may also take occasion to remark that the 1 : 1′-(peri)dibromonaphthalene which formed the object of the investigation by Armstrong and Rossiter referred to above has recently been obtained by me in conjunction with Mr. F. W. Streatfeild from the 1 : 1′-nitronaphthylamine. The melting point of peri-dibromonaphthalene is 108·5—109°. Details concerning this and other peri-di-derivatives will be given when our investigations are more complete.—R. M.

Having recently had occasion to prepare a quantity of the nitrobromonaphthylamine, it appeared worth while to try whether a feebler acid like iodhydric acid would enable the NH_2 group to be replaced by iodine, without at the same time replacing the NO_2 group. The nitrobromonaphthylamine was dissolved in strong sulphuric acid, the solution diluted with a little water, and when cold diazotised in the usual way. The solution of the diazo-salt was filtered into a solution containing the calculated quantity of potassium iodide. Decomposition occurs at ordinary temperatures with the evolution of nitrogen, and the reaction is completed by gently heating for some time till no more gas is evolved. The resinous-looking product was washed with water, and then crystallised repeatedly from alcohol with the addition of animal charcoal. The purified compound consisted of small, ochreous needles, melting at 117—118°. Analysis showed that the desired substitution had taken place:—

0·4819 gram gave 15·3 c.c. moist N at 15·6 and 764·9 mm. bar.
0·2982 „ 0·3344 gram mixed AgBr and AgI.

	Calculated for $C_{10}H_5IBr{\cdot}NO_2$.	Found.
N.....	3·70	3·73
Br + I.....	54·76	54·87

The constitution of this nitrobromoiodonaphthalene is:—



The substance is very readily soluble in benzene, but slightly soluble in petroleum, and freely soluble in hot alcohol, acetone, and glacial acetic acid. By the action of zinc-dust and acetic acid, the compound can be reduced in alcoholic solution, without the removal of halogen, if the solution is kept cool. The base, bromoiodo-β-naphthylamine, is thrown out of the alcoholic solution on dilution with water, in the form of whitish needles, melting when crude at about 89°. The substance soon becomes reddish-brown by oxidation on exposure to the air, and has not therefore been isolated in a state of purity. Its basic character is practically destroyed by the halogen atoms present in the molecule. The acetyl derivative was prepared by heating the solution of the compound in glacial acetic acid with acetic anhydride. After several crystallisations from alcohol, the pure bromoiodo-β-acetonaphthalide was obtained in the form of opaque, white needles, melting at 235°:—

0·2277 gram gave 7·1 c.c. moist N at 20° and 761 mm. bar.

	Calculated for $C_{10}H_5\overset{I(\alpha)}{\underset{Br(\alpha)}{<}}NH\cdot C_2H_3O(\beta)$.	Found.
N	3·59	3·57

The direct replacement having been so easily effected in the case of iodhydric acid, we were led to repeat Prager's work, using Sandmeyer's method. In the first place, the solution of the diazotised nitrobromonaphthylamine was filtered into an excess of cuprous chloride solution, and the reaction completed by heating in the usual manner. The crude product was crystallised several times from alcohol, and finally obtained in the form of ochreous needles, melting at 117°, and possessing all the properties of the preceding compound. A qualitative test showed the presence of nitrogen. Analysis gave the following results:—

0·2922 gram gave 13·7 c.c. moist N at 21° and 759·5 mm. bar.
0·1955 „ 0·2257 gram mixed AgCl and AgBr.

	Calculated for $C_{10}H_5ClBr\cdot NO_2$.	Found.
N	4·89	5·33
Cl + Br	40·32	40·22

The compound can be reduced in cold alcoholic solution with zinc-dust and acetic or even hydrochloric or sulphuric acid, without loss of halogen. The amido-derivative, which is possessed of but very feeble basic properties, separates from the alcoholic solution on dilution with water, in the form of whitish needles. Although somewhat more stable than the corresponding bromoiodo-β-naphthylamine, it also becomes coloured by oxidation on exposure to the air, and has not been obtained as yet in a pure state. A specimen crystallised two or three times from benzene was obtained in the form of brownish, stumpy needles, melting at about 93°. We do not give this melting point as final, as it is proposed to prepare a larger quantity of the substance for future extension of the work. Analysis showed, however, that even at this stage the compound was fairly pure:—

0·1756 gram gave 8·4 c.c. moist N at 18·5° and 766·8 mm. bar.

	Calculated for $C_{10}H_5ClBr\cdot NH_2$.	Found.
N	5·46	5·56

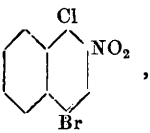
The acetyl derivative was prepared by acetylating in acetic acid

with acetic anhydride. After several crystallisations from dilute alcohol, it formed fine, white needles, melting at 218° :—

0·1474 gram gave 5·9 c.c. moist N at 18° and 765·2 mm. bar.

	Calculated for $C_{10}H_5ClBr\cdot NH\cdot C_2H_3O$	Found.
N	4·69	4·65

By a similar application of Sandmeyer's method, the nitrobromonaphthylamine was converted into dibromonitronaphthalene, which, when pure, forms small, ochreous needles, melting at 117°. The constitution of these last compounds is represented by the formulæ :—



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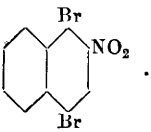

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The results now submitted are sufficient to show that Prager was in error in stating that Sandmeyer's method is inapplicable to the nitrobromonaphthylamine in question. It is proposed to extend the investigation of these compounds in the direction indicated at the outset, and the present note is offered as a preliminary communication, owing to unadvoidable interruption of the work till the autumn.

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